

UDC 546.47'21:539.26

A NEW MODIFICATION OF ZINC OXIDE SYNTHESIZED BY THE HYDROTHERMAL METHOD

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The results of indexing the x-ray diffraction pattern of a new ZnO modification obtained earlier by the hydrothermal method are described. An assumption is made that this is a new high-density modification of ZnO crystallized in a tetragonal volume-centered lattice with $a = 8.572 \text{ \AA}$, $c = 7.186 \text{ \AA}$, and $z = 24$. Its estimated density is 6.215 g/cm^3 .

Several polymorphous modifications of zinc oxide have been discovered. One of them is known as zincite and has the structure of wurtzite (polyhedrons-tetrahedrons ZnO_4 , OZn_4).

The parameters of the hexagonal elementary cell are as follows: $a = 3.2539(1) \text{ \AA}$, $c = 5.2098(3) \text{ \AA}$, $c/a = 1.6011$, $V = 47.77 \text{ \AA}^3$, Fedorov symmetry group $P6_3mc$ (PDF ICPDS 80-0075), experimental density value $5.642(12) \text{ g/cm}^3$, and $z = 2$ [1]. The volume per formula unit (V/z , \AA^3) is 23.89.

The atoms of zinc and oxygen have the equivalent monovariant binary positions $(3m) - 2b$:

Zn – $1/3, 2/3, 0, 2/3, 1/3, 1/2$;

O – $1/3, 2/3, z; 2/3, 1/3, 1/2 + Z$.

For the wurtzite structure with the regular tetrahedron, $c/a = 1.633$ and $Z = 0.375$. In zincite the coordinate Z is somewhat larger: 0.3825(14). Therefore, there is a small difference between one distance Zn – O and the other three: three distances are equal to 1.973 \AA , and the fourth distance is 1.992 \AA [1].

According to a geometric model, the ionic crystal is constructed of incompressible ionic spheres of a certain radius.

Each coordination polyhedron (cube, octahedron, tetrahedron, triangle) has a critical (minimum) ratio of the cation and anion radius r_c/r_a , with which the particular polyhedron can be formed (the anions contact the cations and each other).

For a cube, r_c/r_a is equal to 0.732, for an octahedron 0.414, for a tetrahedron 0.225, and for a triangle 0.155. The probability of a particular coordination of cations can be estimated based on the Magnus-Goldschmidt criterion: a coordination polyhedron is formed in the structure if the ratio r_c/r_a exceeds the critical value. Zinc can have an octahedral environment, since the ratio of the ionic radius of zinc (0.74 \AA) to oxygen (1.33 \AA) is equal to 0.556. The free Gibbs energy in

the modification of coordination $\text{ZnO}_4 \rightarrow \text{ZnO}_6$ calculated by various methods for a number of chemical compounds and solid solutions demonstrates that the tetrahedral coordination is the most probable in zinc. This is also supported by the positive value of the enthalpy of coordination modification ($\text{ZnO}_4 \rightarrow \text{ZnO}_6$) $\Delta H = 24.5 \pm 3.6 \text{ kJ/mole}$ calculated on the basis of thermochemical data [2].

Zinc at atmospheric pressure as a rule has the tetrahedral coordination. A polymorphous transition with a structural modification was registered in zincite at a pressure of 10 GPa and a temperature of 200°C . After the pressure dropped to the atmospheric pressure, a high-pressure phase with the structure of the NaCl type persisted. The Debye crystallogram lines were indexed with $a = 4.280 \text{ \AA}$ [3].

There are four formula units z per elementary cell; the estimated density is 6.892 g/cm^3 , $V = 78.4 \text{ \AA}^3$. The volume per formula unit $V/z = 19.6 \text{ \AA}^3$. The polymorphic transition in zincite is accompanied by a volume jump $\Delta V/V = -17.9\%$. The zinc and oxygen atoms in Fedorov group $Fm3m$ take the positions $4(a) - (000)$ and $4(b) - (1/2, 1/2, 1/2)$. The coordination polyhedrons are ZnO_6 and OZn_6 .

In the study described in [3], the catalyst was NH_4Cl , which at high pressure transforms from a volume-centered structure to a cubic face-centered structure [4]. At a pressure of 0.1 MPa and a temperature of 120°C , the high-pressure phase starts converting into zincite [3].

Zincite is the strongest piezoelectric among the semiconductor materials. Zincite crystals can be synthesized by different methods: synthesis from the gaseous phase (needle-shaped crystals); zinc oxide crystallization from a solution in PbF_2 melt (laminar crystals). However, the properties of the crystals grown using this method do not allow for their application in engineering. The hydrothermal method proved to be more promising for the production of high-quality isometric crystals.

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The crystallization of zincite was studied in detail in chloride and alkaline solutions. The best of the chloride solutions were NH_4Cl solutions (4–10 wt.%). Intense recrystallization in them begins at a temperature of 200°C. However, the size of the grown crystals did not exceed a few millimeters [5].

The study in [6] considered zinc oxide crystals grown in NH_4Cl solutions at a temperature of 450°C and a pressure of 60 MPa. Spontaneous crystallization was carried out on a wire passing along the autoclave axis and on the autoclave walls. With the NH_4Cl content over 4%, long needle-shaped crystals prevailed. Thick prismatic crystals prevailed when the NH_4Cl content in the solution was about 3%. Along with the green prismatic crystals of zincite ZnO , clear laminar crystals were formed as well. It was supposed in [6] that the clear crystals represent a new modification of zinc oxide.

The study in [6] quotes with a low accuracy the Debye crystallograms of the grown zincite crystals and the new ZnO modification. The Debye crystallogram of the new modification of ZnO , except for three lines with interplane distances 2.89, 2.46, and 1.48 Å, were indexed (Table 1) in a triclinic lattice with $a = 3.201$ Å, $b = 3.605$ Å, $c = 2.365$ Å, $\alpha = 102.77^\circ$, $\beta = 90.92^\circ$, $\gamma = 104.76^\circ$, and $V = 25.7$ Å³.

The elementary cell volume differs little from the volume per formula unit in zincite. With $z = 1$, the estimated density is 5.25 g/cm³. There is one zinc atom per cell. Therefore, the x-ray pattern should contain lines with all possible indexes hkl . This is indeed the case (Table 1). For the first seven lines and the ninth line, $M_g = 1165$ and $F_g = 376$.

Using the largest deformation method, it is possible to transform the cubic lattice with $a = 4.280$ Å into a triclinic lattice, whose parameters differ insignificantly from the above listed: $a = 3.210$ Å, $b = 3.549$ Å, $c = 2.393$ Å, $\alpha = 97.75^\circ$, $\beta = 90^\circ$, $\gamma = 107.55^\circ$, and $V = 25.7$ Å³.

The triclinic lattice vectors \vec{A}_{tr} , \vec{B}_{tr} , and \vec{C}_{tr} are related to the cubic lattice vectors \vec{a}_c , \vec{b}_c , and \vec{c}_c by the following dependence:

$$\vec{A}_{\text{tr}} = \frac{1}{2} \vec{a}_c + \frac{1}{4} \vec{c}_c;$$

$$\vec{B}_{\text{tr}} = -\frac{1}{4} \vec{a}_c + \frac{1}{2} \vec{b}_c + \frac{1}{2} \vec{c}_c;$$

$$\vec{C}_{\text{tr}} = -\frac{1}{4} \vec{a}_c - \frac{3}{4} \vec{b}_c + \frac{1}{4} \vec{c}_c.$$

The axis transformation matrix is as follows:

$$\begin{vmatrix} 1/2 & 0 & 1/4 \\ -1/4 & 1/2 & 1/2 \\ -1/4 & -3/4 & 1/4 \end{vmatrix}.$$

It is possible to transit from triclinic lattice I to triclinic lattice II with close parameters a and b : $a = 8.550$ Å,

TABLE 1

Line number	Intensity	Interplanar distance D_c , Å	Triclinic lattice			
			I		II	
			hkl	D_v , Å	hkl	D_v , Å
1	1	3.390	010	3.390	$\begin{cases} 201 \\ -1-21 \end{cases}$	$\begin{cases} 3.393 \\ 3.390 \end{cases}$
2	3	3.110	100	3.086	$\begin{cases} 2-20 \\ 211 \end{cases}$	$\begin{cases} 3.096 \\ 3.086 \end{cases}$
3	2	2.890	—	—	$\begin{cases} 112 \\ -212 \\ -221 \\ 003 \end{cases}$	$\begin{cases} 2.914 \\ 2.880 \\ 2.861 \\ 2.860 \end{cases}$
4	10	2.660	1-10	2.659	$\begin{cases} 130 \\ -2-22 \\ -103 \end{cases}$	$\begin{cases} 2.660 \\ 2.471 \\ 2.470 \end{cases}$
5	5	2.460	—	—	$\begin{cases} -302 \\ 003 \end{cases}$	$\begin{cases} 2.446 \\ 2.446 \end{cases}$
6	2	2.300	001	2.300	$\begin{cases} 230 \\ 0-32 \\ -203 \\ -3-21 \end{cases}$	$\begin{cases} 2.301 \\ 2.300 \\ 2.300 \\ 2.291 \end{cases}$
7	3	2.150	0-11	2.150	$\begin{cases} -322 \\ 040 \\ 113 \end{cases}$	$\begin{cases} 2.150 \\ 2.146 \\ 2.143 \end{cases}$
8	1	2.030	110	2.030	$\begin{cases} 1-23 \\ -141 \\ -303 \\ -2-23 \end{cases}$	$\begin{cases} 2.032 \\ 2.031 \\ 2.030 \\ 2.030 \end{cases}$
9	5	1.910	-101	1.916	$\begin{cases} -4-12 \\ -241 \\ 4-11 \end{cases}$	$\begin{cases} 1.916 \\ 1.916 \\ 1.910 \end{cases}$
10	5	1.680	1-20	1.686	$\begin{cases} 500 \\ 114 \\ -304 \end{cases}$	$\begin{cases} 1.680 \\ 1.679 \\ 1.678 \end{cases}$
11	9	1.570	2-10	1.570	$\begin{cases} -2-43 \\ 2-14 \\ 5-11 \end{cases}$	$\begin{cases} 1.572 \\ 1.571 \\ 1.570 \end{cases}$
12	6	1.480	—	—	$\begin{cases} -442 \\ -4-33 \\ -1-15 \end{cases}$	$\begin{cases} 1.482 \\ 1.482 \\ 1.477 \end{cases}$
13	6	1.350	120	1.343	$\begin{cases} 234 \\ 2-61 \\ 0-62 \\ -434 \end{cases}$	$\begin{cases} 1.352 \\ 1.351 \\ 1.351 \\ 1.351 \end{cases}$
14	1	1.170	0-12	1.175	$\begin{cases} 235 \\ 353 \\ -5-25 \end{cases}$	$\begin{cases} 1.171 \\ 1.171 \\ 1.169 \end{cases}$

$b = 8.602$ Å, $c = 7.461$ Å, $\alpha = 91.66^\circ$, $\beta = 101.17^\circ$, and $\gamma = 93.10^\circ$. The matrix of transition to lattice II is

$$\begin{vmatrix} 1 & 1 & 3 \\ -2 & -1 & 2 \\ -1 & 2 & 0 \end{vmatrix}.$$

All lines of the new ZnO modification are indexed in lattice II.

TABLE 2

Line number	Tetragonal lattice		Rhombic lattice	
	<i>hkl</i>	<i>D_v</i> , Å	<i>hkl</i>	<i>D_v</i> , Å
1	121	3.382	102	3.388
2	112	3.091	220	3.086
3	{220 022}	3.038 2.752	030	2.865
4	031	2.655	031	2.669
5	{131 003}	2.536 2.395	003	2.444
6	013	2.307	302	2.301
7	040	2.143	{040 410}	2.149 2.146
8	123	2.031	322	2.028
9	240	1.917	223	1.916
10	150	1.681	024	1.686
11	143	1.570	342	1.570
12	{134 350}	1.497 1.470	252	1.469
13	{260 125}	1.355 1.346	612	1.353
14	453	1.169	{552 245 216}	1.170 1.168 1.167

One of the criteria pointing to a higher symmetry is the coincidence of a significant number of lines with various *hkl* indexes. This is in fact observed in indexing the x-ray pattern of ZnO in lattice II parameters.

The indexing results shown in Table 1 indicate that there are two indexing variants (Table 2) in higher-symmetry lattices: a primitive rhombic lattice ($a = 8.865$ Å, $b = 8.595$ Å, $c = 7.332$ Å, $V = 559$ Å³) and a tetragonal one ($a = 8.572$ Å, $c = 7.186$ Å, $V = 528$ Å³).

If we regard the fifth line of the x-ray pattern of the new ZnO modification with interplanar distance 2.46 as consisting of two lines, then all x-ray pattern lines of the new ZnO modification are indexed in a tetragonal volume-centered lattice (Table 2).

With $z = 24$, the estimated density for the rhombic lattice is 5.806 g/cm³, and for the tetragonal one it is 6.215 g/cm³.

Crystallization of zincite in hydrothermal conditions often proceeds in a reducing medium due to the formation of hydrogen caused by oxidation of the autoclave walls under the effect of water and especially alkalis. The pressure of hydrogen in using alkalis reaches 6–8 MPa [7].

Ionic compounds and minerals exhibit the perfect isovalent isomorphism between bivalent iron (0.74 Å) and zinc in sphalerites.

The green tint of zincite crystals grown in the experiment described in [6] is probably determined by the incorporation of the chromophore bivalent iron ion in the crystal lattice.

The preference enthalpy of Fe²⁺ ions for the octahedral positions in the oxygen environment compared to the tetrahedral positions $\Delta H = -26.4$ kJ/mole. Accordingly, one can suppose that bivalent iron ions are arranged in the octahedral vacancies of the zincite structure. When a denser phase of ZnO is formed, Fe²⁺ ions will be “squeezed out” of the crystal.

All this suggests that Rikl and Bauer [6] have grown clear crystals of the new high-density modification of ZnO with a tetragonal lattice: $a = 8.572$ Å and $c = 7.186$ Å.

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